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# Phosphorus Loading from the Redwood River Basin: Fractionation of Labile and Refractory Components

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**PURPOSE:** The purpose of this demonstration effort was to quantify loading of labile and refractory phosphorus fractions from the agriculturally dominated Redwood River Basin, which drains into the Minnesota River. This information will be important for future calibration and verification of watershed models that forecast the impacts of best management practices (BMP's) on water quality and runoff.

**BACKGROUND:** The Minnesota River contributes substantial water, sediment, and nutrient incomes to the Upper Mississippi River (UMR) system, due primarily to intensive agricultural land use that has increased throughout the watershed over the past few decades. Soil and nutrient erosion from the watershed is exacerbated by accelerated runoff due to increased row cropping within the flood plain, extensive agricultural surface and subsurface drainage networks to more rapidly drain soils for corn production, channelization of tributaries and ditches, and increased urbanization. As a result of these watershed modifications, the Minnesota River has become an important element of the budget of the UMR, dominating annual loadings of suspended sediment, nitrogen, and phosphorus (James, Barko, and Eakin 1999). These inputs are contributing considerably to deteriorating water quality and loss of aquatic habitat both in the Minnesota River and the UMR. In particular, much of the sediment and nutrient loads delivered to the UMR by the Minnesota River are being intercepted by the various pools and backwater regions formed by locks and dams on the UMR, thus accelerating eutrophication and sedimentation in these important aquatic and waterfowl habitats (James, Barko, and Eakin 1999).

Although much research in recent years has been devoted to quantifying sediment and nutrient loads from the Minnesota River and its various tributaries (Minnesota Pollution Control Agency (MPCA) 1993a, 1993b; Metropolitan Waste Control Commission (MWCC) 1993), nothing is known about the composition of various labile and refractory phosphorus pools being discharged by these inflows and their potential reactivity with the water column via kinetic exchanges and equilibrium processes (adsorption-desorption), redox reactions, and biological breakdown processes. In addition, no information exists to link watershed-derived transport of phosphorus pools from tributary inflows to the Minnesota River with the regulation of soluble phosphorus concentrations at downstream locations in the UMR. Thus, there is a need to identify loading of various phosphorus pools from tributaries of the Minnesota River for incorporation into eutrophication and watershed loading models (i.e., HSPF; CASC2D) to develop predictive capabilities for examining phosphorus sources and fates in the Minnesota River and UMR under different management and operational scenarios. In particular, management decisions regarding project operations and BMP's along the Minnesota River to reduce the impacts of suspended sediment on water quality and phosphorus concentrations will be derived from an evaluation of loadings of various particulate and soluble phosphorus pools.

As part of the Land Management System (LMS) initiative of the Corps of Engineers, this effort examined loadings of various labile and refractory phosphorus pools and phosphorus adsorption-desorption kinetics for runoff from the Redwood River basin. This watershed of the Minnesota River was chosen because its land use characteristics are dominated by intensive agricultural practices (row cropping, tiling, etc.). Information from this research will be used to calibrate and refine the Watershed Modeling System (WMS) for forecasting changes in loading under different management and operational scenarios.

**METHODS:** A water sampling station was established on the Redwood River at an existing U.S. Geological Survey flow gauging station located near Redwood Falls, MN (Figure 1). In 1999, water samples were collected on a flow-weighted basis during storm inflows using automated water samplers (ISCO models 6700 and 3700) and stage height recorders (ISCO model 750). Samples were retrieved from the field (8-hr round trip) for processing within 3 days of initial sampling. In the laboratory, individual samples were composited into a daily sample for analysis.

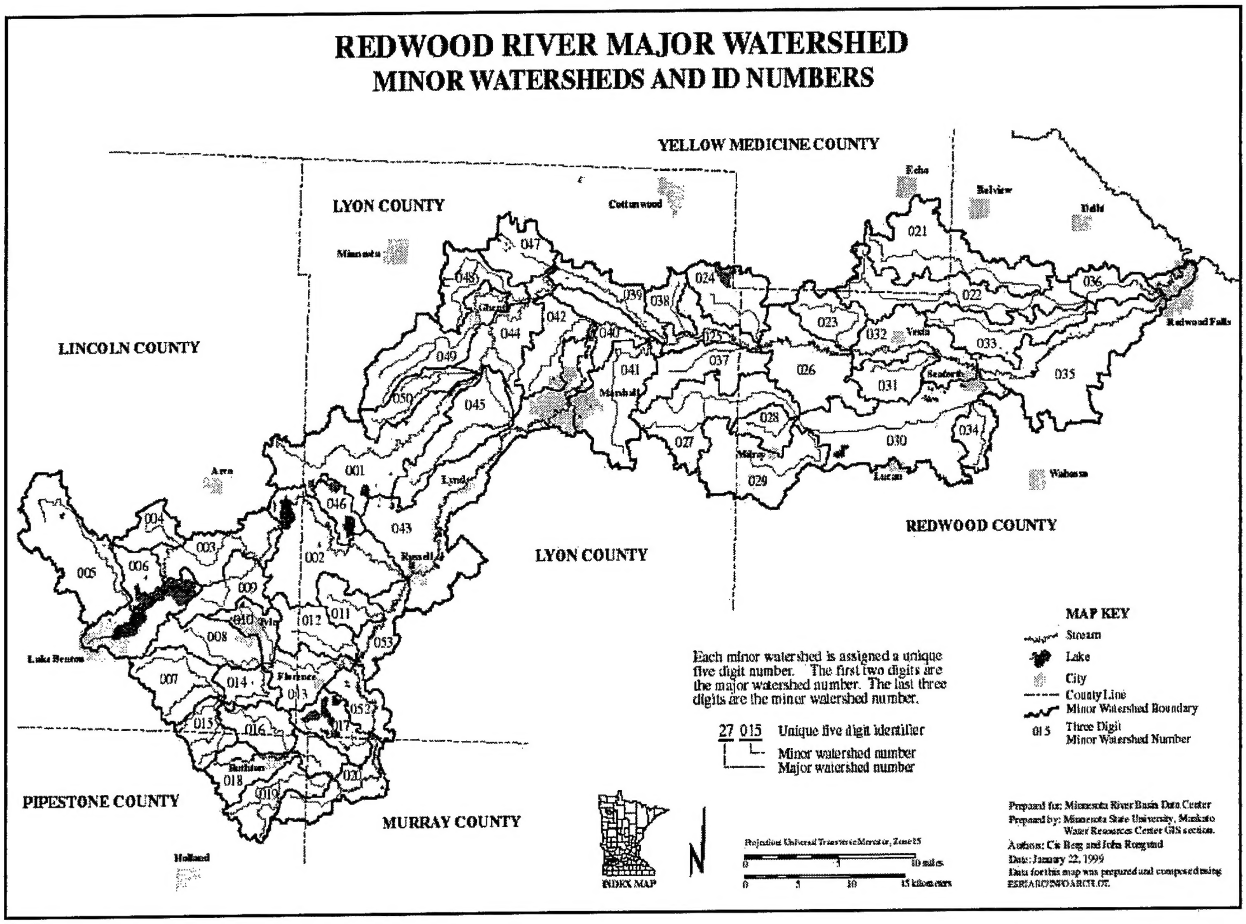


Figure 1. Redwood River Basin. The sampling station was located in Redwood Falls

Shortly after compositing samples, a portion was filtered through a 0.45-µm filter for soluble constituent determination. Soluble reactive phosphorus was analyzed using automated analytical techniques (Lachat Method 10-115-01-1-A; Lachat Quikchem Autoanalyzer, Zellweger

Analytics, Lachat Div., Milwaukee, WI). For particulate components, another sample portion was retained on glass fiber filters (Gelman Metricel). For total suspended sediment (TSS) and particulate organic matter (POM), suspended material was dried at 105 °C to a constant weight, then combusted at 500 °C for 1 hr (American Public Health Association (APHA) 1992). Sequential fractionation of inorganic phosphorus in the sediments was conducted according to Hieltjes and Lijklema (1980) and Nürnberg (1988) for the determination of ammonium-chloride-extractable phosphorus (i.e., loosely bound phosphorus), bicarbonate-dithionite-extractable phosphorus (i.e., iron-bound phosphorus), sodium hydroxide-extractable phosphorus (i.e., aluminum-bound phosphorus), and hydrochloric acid-extractable phosphorus (i.e., calcium-bound phosphorus). A subsample of the NaOH extract was digested with potassium persulfate to determine nonreactive NaOH-extractable phosphorus (Psenner and Puckso 1988). Labile organic phosphorus was calculated as the difference between reactive and nonreactive NaOH extractable phosphorus. Each extraction was filtered through a 0.45-µm filter, adjusted to pH 7, and analyzed for soluble reactive phosphorus. See Table 1 for a listing of the various phosphorus fractions. Particulate phosphorus concentrations were analyzed colorimetrically using Lachet QuikChem procedures (Lachet Method 13-115-06-1-B) following digestion with sulfuric acid, potassium sulfate, and red mercuric oxide (Plumb 1981). Samples for total nitrogen and phosphorus were predigested with alkaline potassium persulfate according to Ameel, Axler, and Owen (1993) before analysis using automated analytical procedures (see above).

**Table 1**
**Operationally Defined Phosphorus Fractions in the Study**

| Operationally Defined P Fraction | Reactivity with the Water Column |
|---|---|
| Loosely Bound P (Interstitial P, $CaCO_3$-P, loosely sorbed P) | Labile |
| Iron-Bound P | Labile |
| Aluminum-Bound P | Refractory |
| Labile Organic P (Labile organic P and polyphosphates) | Labile |
| Calcium-Bound P (Apatate P) | Refractory |
| Refractory Organic P | Refractory |

To measure phosphorus sorption characteristics of TSS loads from the Redwood River Basin, several daily composited samples were combined into one sample representing a storm hydrograph. This sample was centrifuged at 2500 rpm for 30 min and decanted to separate particulate from soluble phases. Sediment aliquots (~500 mg/L dry weight equivalent) were subjected to a series of soluble reactive phosphorus ($KH_2PO_4$ as SRP) standards ranging from 0 to 1.0 mg/L (i.e., 0, 0.125, 0.250, 0.500, and 1.00 mg/L) for examination of phosphorus adsorption and desorption over a 24-hr period. The concentration of suspended sediment used in the study fell within the upper range of concentrations occurring naturally in the Redwood River basin during periods of elevated inflow (see Figure 2). Untreated tap water from the laboratory was used as the water medium because it was phosphate-free and exhibited cationic strength, conductivity, and pH very similar to that of surface water from the Redwood River. Chloroform (0.1 percent) was added to inhibit biological activity. The sediment systems, containing sediment, tap water, and known concentrations of SRP, were shaken uniformly for 24 hr, then

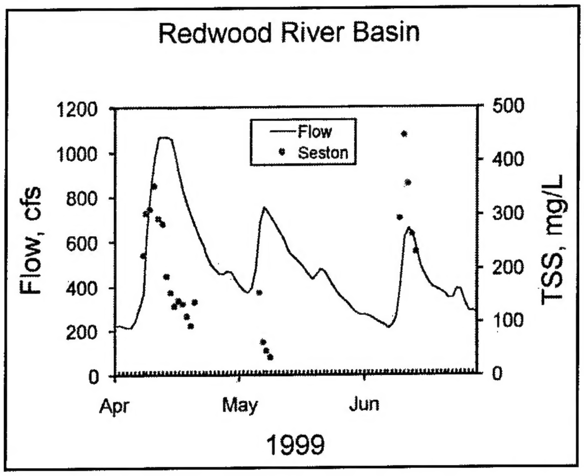


Figure 2. Variations in flow and total suspended sediment concentrations for the period April through June

sampled and analyzed for SRP (APHA 1992). The sediment systems were maintained under oxic conditions at a pH of approximately 8.0 to 8.3 and a temperature of approximately 20 °C .

Adsorption and desorption were calculated as the change in SRP (i.e., SRP at 0 hr minus SRP at 24 hr) normalized with respect to sediment dry mass (i.e., mg SRP/g dry mass) and plotted as a function of final SRP concentration (Froelich 1988). The equilibrium phosphate concentration (EPC, mg/L) was calculated as the concentration where net sorption was zero (i.e., often called the crossover point (Mayer and Gloss (1980)). The linear adsorption coefficient (LAC, L/g) was calculated as the linear slope near the EPC. The native adsorbed phosphate (NAP, mg/g sediment) was calculated as NAP = (LAC)(EPC).

## RESULTS

**Phosphorus Composition of Runoff.** A series of storm-related inflows from the Redwood River Basin are shown for the period April through June in Figure 2. During that seasonal period, peaks in the hydrograph occurred in mid-April, early May, and early June. During each storm inflow, the hydrograph was characterized by a rapid rise in flow to a maximum, followed by a gradual decline in flow that lasted several weeks (more than 3 weeks). TSS concentrations exhibited a hysteresis effect, as they increased markedly during the rising limb of the hydrograph and started declining through the peak and trailing limb of the hydrograph.

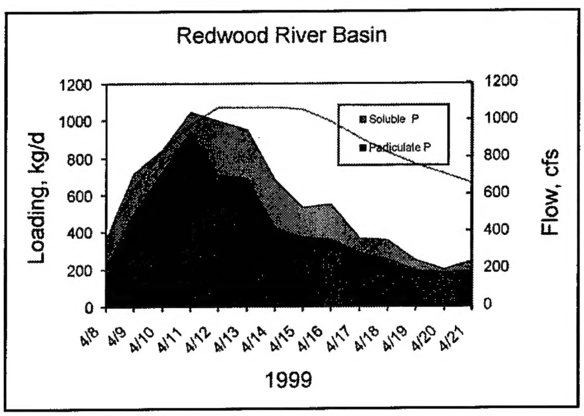


Figure 3. Variations in total phosphorus loading and the proportion that is in soluble and particulate forms (different colored areas) during a storm inflow in April 1999

The storm inflow occurring in mid-April provided a typical example of the pattern of loading of particulate and soluble phosphorus constituents (Figure 3) from the Redwood River Basin. During that storm-related period, total phosphorus loading exhibited a maximum prior to the peak in the hydrograph, similar to patterns observed for TSS. Particulate phosphorus fractions accounted for most of the phosphorus load from the watershed (Figure 3). The particulate phosphorus load was dominated by inorganic phosphorus fractions, as particulate organic phosphorus fractions accounted for less than 30 percent of the particulate phosphorus load (Figure 4). The loosely bound and iron-bound phosphorus fraction accounted for

approximately 60 percent of the particulate inorganic phosphorus load during this storm event (Figure 5). More refractory calcium-bound and aluminum-bound phosphorus accounted for approximately 40 percent of the particulate inorganic phosphorus load (Figure 5).

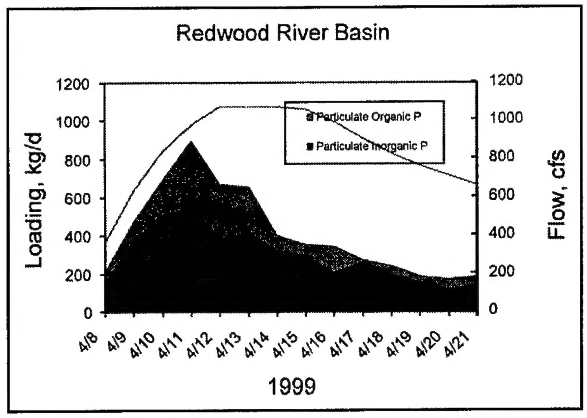


Figure 4. Variations in particulate phosphorus loading and the proportion that is in organic and inorganic forms (different colored areas) during a storm inflow in April 1999

The overall composition of phosphorus loads from the Redwood River Watershed for the period April through June is shown in Figure 6. Labile sediment phosphorus fractions (particulate labile organic phosphorus, loosely bound phosphorus, and iron-bound phosphorus) and soluble fractions (SRP and soluble unreact phosphorus (SUP)) collectively accounted for 75 percent of the total phosphorus load during this period. Refractory phosphorus forms (Aluminum-bound phosphorus, refractory organic phosphorus, and calcium-bound phosphorus) collectively accounted for 25 percent of the total phosphorus load during this period.

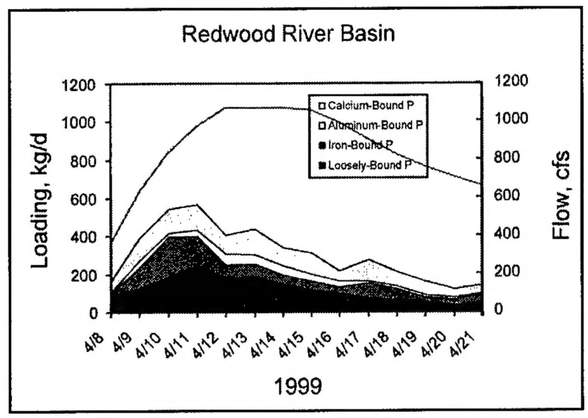


Figure 5. Variations in particulate phosphorus loading and the proportion that is loosely bound, iron-bound, aluminum-bound, and calcium-bound (different colored areas) during a storm inflow in April 1999

**Sorption Characteristics of TSS Loads.** At low ambient SRP, TSS loads originating from the Redwood River watershed desorbed phosphorus, based on laboratory sorption experiments (Figure 7). As ambient SRP increased, SRP was adsorbed onto particulate fractions. The EPC was relatively high at 0.074 mg P/L, compared to other studies (Meyer 1979, Mayer and Gloss 1980, studies cited in Froelich (1988), Olila and Reddy 1993), and the high k of these sediments suggested a high buffering capacity for soluble phosphorus when concentrations were near the EPC (Figure 7). The EPC of sediments originating from the Redwood River watershed was also similar to flow-weighted concentrations of SRP (Figure 6).

**DISCUSSION:** Analysis of total phosphorus loading alone does not provide information regarding phosphorus availability to biota or the potential for recycling through sediment-water interactions as it is transported to downstream locations. Our results suggested that during the period of study, up to 75 percent of the phosphorus load originating from the watershed was in labile form (i.e., subject to transformations which make it available for uptake by biota) while 25 percent of it was in refractory form (i.e., subject to permanent burial). Thirty percent of the labile phosphorus fraction was in soluble form and available for algal uptake and growth (i.e., SRP and SUP). SRP was directly available for algal uptake while SUP can be converted to

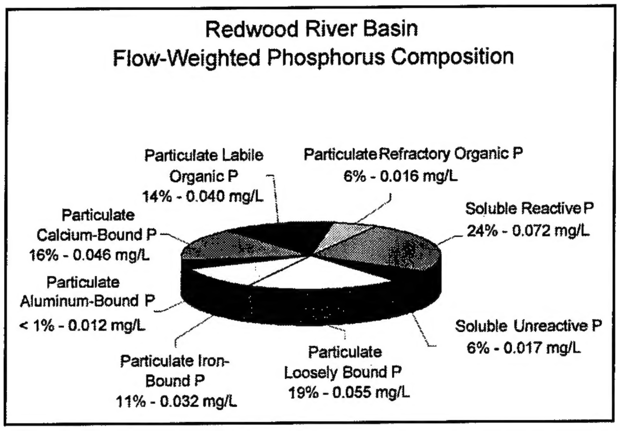


Figure 6. Flow-weight phosphorus composition for the period April through June 1999

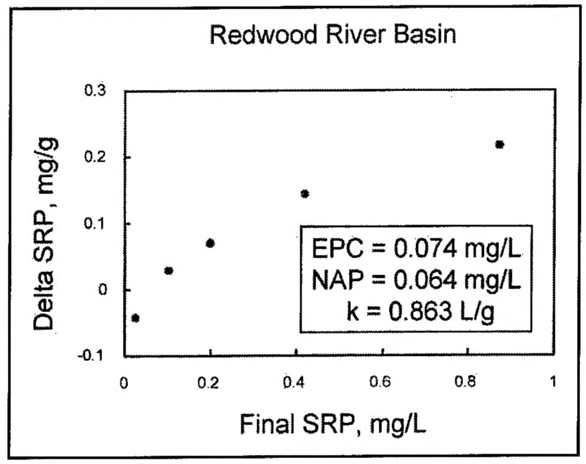


Figure 7. Sorption characteristics for suspended sediment collected during a high inflow event in April. EPC = Equilibrium phosphate concentration, NAP = Native adsorbed phosphorus, k = linear sorption coefficient. Final SRP represents the aqueous phosphorus concentration. Delta SRP represents sorption (positive value) or desorption (negative value)

available forms via enzymatic (i.e., alkaline phosphatase activity; Franko and Heath 1979; Pettersson 1980) and UV light reactions (Franko and Heath 1982).

The other 45 percent of the labile fraction was bound to sediment or organic matter and could become available to the biota through various recycling pathways. For instance, inorganic labile phosphorus could become directly available to biota via kinetic processes (i.e., adsorption-desorption). For the period April through June, it appeared that kinetic processes potentially played an important role in regulating soluble phosphorus concentrations in the runoff from the Redwood River Basin. The EPC of suspended sediment, determined from sorption studies conducted in the laboratory, was very similar to the ambient concentration of SRP in the runoff. This pattern, coupled with a high ratio of particulate to soluble phosphorus in the runoff, suggested that sorption processes with particulate phosphorus were buffering aqueous phases of phosphorus.

The loosely bound (Boström 1984) and iron-bound (Nürnberg 1988) labile phosphorus fraction are readily mobilized as a result of oxidation-reduction reactions (Mortimer 1971). This mechanism of phosphorus flux may be a very important element in the phosphorus economy of downstream reservoirs located on the Minnesota and Mississippi Rivers, which ultimately trap a large portion of these suspended sediment loads. In particular, up to 80 percent of the TSS load to Lake Pepin, Upper Mississippi River, is stored in the lake (James, Barko, and Eakin 1999). Most of this sediment, having its origins in the Minnesota River Basin, exhibits high rates of phosphorus release under both oxic and anoxic conditions (2.9 and 14.5 $mg/m^{-2}/d^{-1}$, respectively; James, Barko, and Eakin 1999).

In conclusion, using operationally defined fractionation procedures, labile and refractory phosphorus components were identified in the runoff from the Redwood River Basin. A very

high proportion of the phosphorus load from the watershed consisted of labile phosphorus fractions, which can be used by biota for growth in downstream locations of the Minnesota and Mississippi Rivers. This information will be important in the evaluation of BMP's for improving water quality and reducing runoff of constituents from the Redwood River Basin that potentially contribute to downstream eutrophication and poor water quality.

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*www.wes.army.mil/el/pubs/wqtncont.html*

## REFERENCES

Ameel, J. J., Axler, R. P., and Owen, C. J. (1993). "Persulfate digestion for determination of total nitrogen and phosphorus in low nutrient waters," *Am. Environ. Lab.*, 8-10.

American Public Health Association. (1992). *Standard methods for the examination of water and wastewater.* 18th ed.

Boström, B. (1984). "Potential mobility of phosphorus in different types of lake sediment," *Int. Rev. Ges. Hydro.* 69, 457-474.

Franko, D. A., and Heath, R. T. (1979). "Functionally distinct classes of complex phosphorus compounds in lake water," *Limnol. Oceanogr.* 24, 463-473.

Franko, D. A., and Heath, R. T. (1982). "UV-sensitive complex phosphorus: Association with dissolved humic material and iron in a bog lake," *Limnol. Oceanogr.* 27, 564-569.

Froelich, P. N. (1988). "Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism," *Limnol. Oceanogr.* 33, 649-668.

Hieltjes, A. H., and Lijklema, L. (1980). "Fractionation of inorganic phosphorus in calcareous sediments," *J. Environ. Qual.* 8, 130-132.

James, W. F., Barko, J.W., and Eakin, H. L. (1999). "Diffusive and kinetic fluxes of phosphorus from sediments in relation to phosphorus dynamics in Lake Pepin, Upper Mississippi River," Miscellaneous Paper W-99-1, Engineer Research and Development Center, Waterways Experiment Station, Vicksburg, MS.

Mayer, L. M., and Gloss, S. P. (1980). "Buffering of silica and phosphate in a turbid river," *Limnol. Oceanogr.* 25, 12-25.

Meyer, J. L. (1979). "The role of sediments and bryophytes in phosphorus dynamics in a headwater stream ecosystem," *Limnol. Oceanogr.* 24, 365-375.

Mortimer, C. H. (1971). "Chemical exchanges between sediments and water in the Great Lakes - Speculations on probable regulatory mechanisms," *Limnol. Oceanogr.* 16, 387-404.

Minnesota Pollution Control Agency. (1993a). "Mississippi River phosphorus study, Section 3: Lake Pepin water quality: 1976 – 1991," Water Quality Division, St. Paul, MN.

Minnesota Pollution Control Agency. (1993b). "Mississippi River phosphorus study, Section 7: Lake Pepin and Mississippi River bathtub modeling," Water Quality Division, St. Paul, MN.

Metropolitan Waste Control Commission. (1993). "Mississippi River Study. Section 3. Description of study area: Water Quality of the Mississippi River and Tributaries, 1976-1991," Water Quality Division, St. Paul, MN.

Nürnberg, G. K. (1988). "Prediction of phosphorus release rates from total and reductant soluble phosphorus in anoxic lake sediments," *Can. J. Fish. Aquat. Sci.* 44, 960-966.

Olila, O. G., and Reddy, K. R. (1993). "Phosphorus sorption characteristics of sediments in shallow eutrophic lakes of Florida," *Arch. Hydrobiol.* 129, 45-65.

Pettersson, K. (1980). "Alkaline phosphatase activity and algal surplus phosphorus as phosphorus deficiency indicators in Lake Erkin," *Arch. Hydrobiol.* 89, 54-87.

Plumb, R. H. (1981). "Procedure for handling and chemical analysis of sediment and water samples," Tech Rep. EPA/CE-81-1, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Psenner, R., and Puckso, R. (1988). "Posphorus fractionation: Advantages and limits of the method for the study of sediment P origins and interactions," *Arch. Hydrobiol. Biel. Erg. Limnol.* 30, 43- 59.